FINAL CORE REPORT (PUBLIC)

This project was carried out with a subsidy from the Ministry of Economic Affairs and Climate, subsidy scheme Top Sector Energy, carried out by RVO.

Project Title:	Core: Co-Fluid Catalytic Cracking of Pyrolysis Liquids in Existing Refineries (CoRe)), reference number TBBE119011.
Project leader(s):	Prof. Dr. ir. H.J. Heeres, Prof. Dr. B.M. Weckhuysen, Dr. Ir. R.H. Venderbosch
Affiliation(s):	University of Groningen, University of Utrecht and BTG B.V.
Researcher(s) employed	Dr. S. He (RUG), Dr. Balaji Sridharan (RUG), Dr. N. Nikolopoulos (UU)

1. Project & results

Aims and objectives of the research project

The research carried out in the CORE project framework entails the co-feeding of pyrolysis oils into existing oil refineries. This idea has been embraced by companies such as Preem, which plans to replace a portion of the fossil inputs in an oil refinery with pyrolysis oil from among others BTG-BTL. The FCC (Fluid Catalytic Cracking) unit is considered the best entry point for introducing pyrolysis oil into the refinery. However, several questions must be answered to improve feasibility and reduce risk. For example, it is unclear how much oil can be blended without jeopardizing the refining process and how long the catalysts can withstand contaminants from the biomass (e.g., alkalis). A partially pretreated pyrolysis oil performs better, but it is unclear to what extent the oil needs to be treated. The problem is that there are no lab-scale units for co-feeding pyrolysis oil. The activities performed in this project are aimed at partially removing these barriers, and the goals are:

- Design and operate an experimental setup to provide reliable data on a small scale;
- Gaining fundamental insights into and increasing the comfort level of co-feeding;
- Developing models for techno-economic evaluations.

The activities were divided into 3 scientific WP's:

1. Design, construction, and operation of an innovative experimental unit to test the co-feeding technology at a lab scale
2. Development of improved catalysts and fundamental knowledge regarding catalyst performance
3. Developing strategies and concept, with related challenges and models, for integrating bio-liquids into existing refineries.

New insights and remarkable scientific results, bottlenecks and setbacks

A detailed overview of the results is given in the technical report which is attached to this report. Based on the research activities employed, we can conclude that:

- We have designed and constructed an innovative, dedicated experimental set-up mimicking an FCC unit that is suitable for co-feeding VGO with (stabilized) bioliquids
- Successful tests were carried out on the co-feeding of VGO and a representative bioliquid at TRL-4.
- The design of the unit was the basis for a patent: Laboratory scale fluid catalytic cracking unit for co-refining bio-based feedstocks.
- The results of the project were used as background information for a granted Horizon Horizon Europe Innovation Action "REFOLUTION"
- One of the post-docs hired for the project (S. He) started a company among others to license the co-FCC technology developed in the project to third parties
- Novel-shaped catalysts were developed for co-FCC applications of VGO and bioliquids
- Collect data to summarize the effects of PL processing in refineries.

Bottlenecks

The COVID pandemic led to severe delays in the execution of the project as:

- Lab access was restricted at all locations for extended periods
- Physical progress meetings were not possible
- Delivery of essential hardware and particularly those for process control of the units (e.g. PLC units) was heavily delayed

In addition, the original unit was intended to be located at the premises of the University of Groningen. Unfortunately, this proved not possible as i) the unit was larger than anticipated and did not fit in the lab space in Groningen and ii) foreseen moving of the labs in Groningen to a new building (Feringa building) with even less space for larger units. It was decided to construct and operate the unit at the premises of BTG in Enschede. This caused some additional delays due to among others infrastructure modifications and very strict safety policies requiring hardware and control modifications at BTG.

2. Valorization

There is a strong need to obtain reliable information on the effects of co-feeding bioliquids in existing oil refineries on operability and product portfolio. This particularly goes for the FCC unit in an oil refinery, which is considered a very good entry point for bioliquids. However, lab scale equipment to mimic the performance of FCC units for VGO alone and VGO/bioliquids for obtaining reliable information for scale-up purposes is non-existent. Typically MAT units based on GC techniques are used at the lab scale, and although the output gives guidelines, it is not representative of FCC units. Pilotscale FCC equipment is available (DCR), but is less suitable to be used in a lab environment and is investment expensive (> 1 Meuro). To fill the gap, we proposed to develop a co-FCC unit at a lab scale that is suitable to provide reliable scale-up data.

The unit has been designed, built, and commissioned and the first experimental tests have been performed using VGO and VGO in combination with a bioliquid (a hydrotreated pyrolysis liquid, HPO). Based on the results, a patent application has been filed for the unit. The know-how generated in the project and IP protection has been used to:

a. Start a company (CorePro) that will sell the co-FCC unit to interested companies under a license from the University of Groningen

b. Become a partner in a recently granted EU Horizon research project (REFOLUTION Grant Agreement N° 101096780). Here, the unit will be used to test the co-feeding of specific bioliquids with VGO.

Data and knowledge generated from this project have been applied for both exploitation activities and were instrumental.

3. Output

Poster/presentations:
-

Publications:
In progress, at least one is foreseen

Patents:
Laboratory scale fluid catalytic cracking unit for co-refining bio-based feedstocks.

4. Follow-up

Career staff:

a. Dr. B. Sridharan (RUG), one of the post-docs hired for the project, is now employed at VITO, Belgium as a post-doctoral fellow.
b. Dr. S. He, now owner of a company (Corepro), with among others the task to licence the co-fcc technology developed in the project to external companies
c. Dr. N. Nikolopoulos (UU): current employer unknown

The research activities will be continued in the framework of an EU Horizon project 'REFOLUTION', with both BTG and RUG as partners.

One of the post-docs hired for the project (S. He) started a company among others to license the co-FCC technology developed in the project to third parties.

5. Results for the general public

Greening the Dutch economy is directly linked to the ongoing climate debate and the desired biobased and circular transition. The main source of renewable carbon is biomass. Biomass can be used for energy generation (e.g., co-firing biomass in power plants) but also for higher-value applications such as transportation fuels and basic and fine chemicals. Among the technologies for converting biomass into higher-value products, pyrolysis is one of the most interesting. Pyrolysis has advanced significantly in recent years, and the Netherlands is a world leader in this field with companies like BTG and BTG-BTL Bioliquids. The technology applies to a wide range of biomass and is also useful for lower-value biomass like agricultural residues. However, the primary product, liquid pyrolysis oil, is not directly usable as a transportation fuel and requires further processing for commercial applications. The CoRe project focused on valorizing pyrolysis oil in existing oil refining units and converting it, through catalytic cracking (FCC) with crude oil, into an existing pool of fuels and bulk chemicals. For this purpose, a dedicated experimental set-up has been designed, built and commissioned. A company is founded, among others to license the co-FCC technology developed in the project to third parties.

Technical report

1. Design, construction and operation of an innovative experimental unit to test the co-feeding technology at lab scale

1.1. General features

We have selected a downflow reactor (downer) to mimic Fluid Catalytic Cracking (FCC) as done in the industry. The downer system has certain advantages compared to conventional upflow operation such as reduced back mixing of catalyst and vapors. This makes the residence time distribution in a downer reactor narrower compared to a riser and hence, higher selectivity towards desired products and lower yield of undesired products are expected. A start for the design is the set-up described by researchers in the group of Corma (see Figure 1).

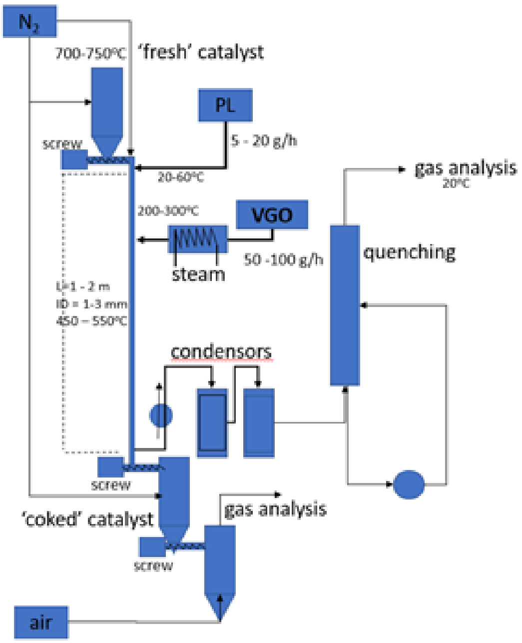


Figure 1. Downer FCC unit as proposed by Corma.

This design has been taken as the basis and modified considerably by (Figure 2):
i) use of dedicated transport systems for the catalysts from the downer, as opposed to dip legs in the original design.
ii) VGO and bioliquids may be fed separately, at positions chosen along the downer length.
iii) the implementation of a catalyst recycle option instead of once through operation. This involves transport of the spend catalyst to a combustor where the catalyst is regenerated.

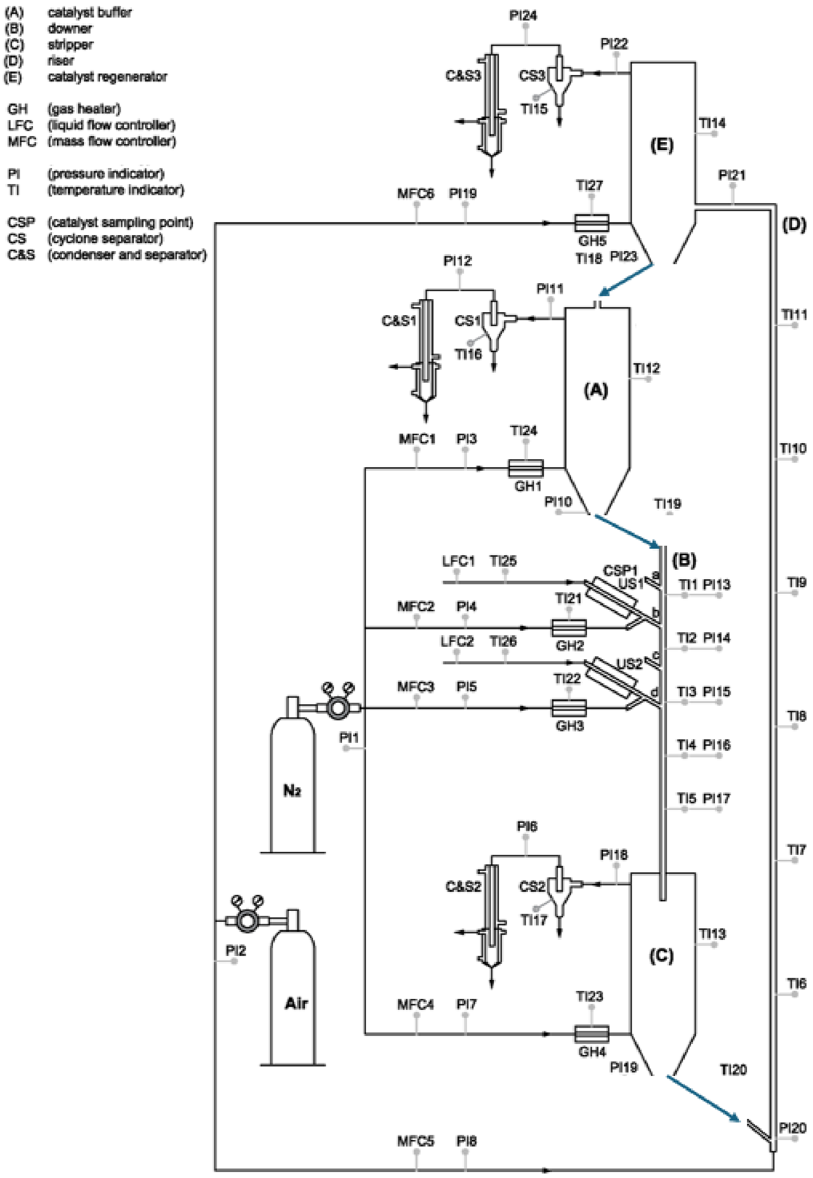


Figure 2. Schematic representation of the design of the labscale co-FCC unit

The unit is very flexible concerning process condition variations for instance, the catalyst residence times may be varied between 1 and 10 s, and temperatures from 450 to 550°C in the downer. A detailed description of the unit and the individual subunits is given in Appendix 1.

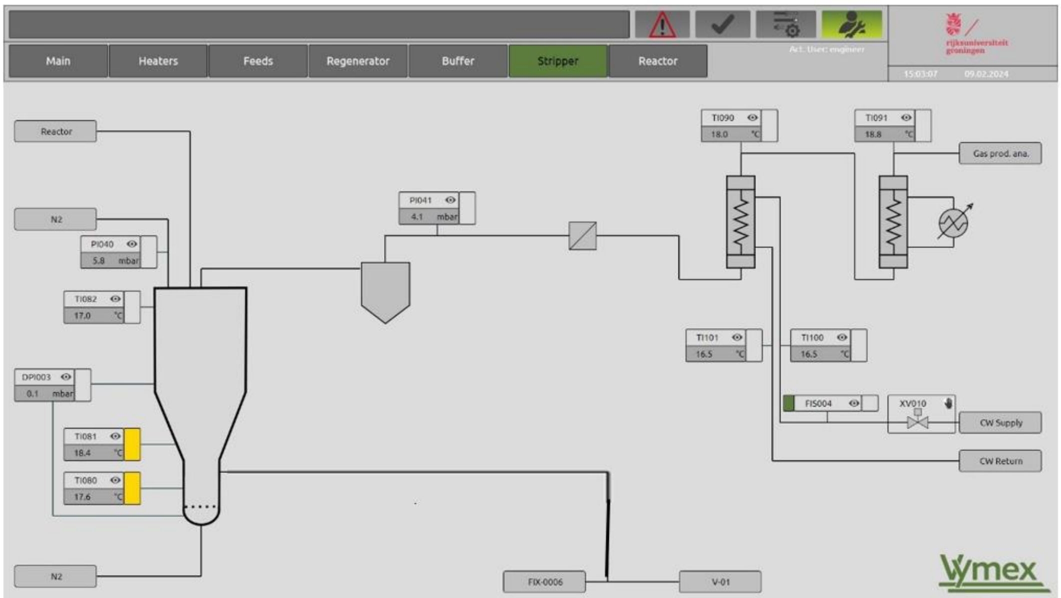
1.2 Construction of the unit

The lab-co-FCC unit has been built at the premises of BTG. Several images are given below to show parts of the unit.

Figure 3. Representative images of the co-FCC unit.

1.3 Commissioning of the unit

Extensive cold-flow testing was performed to check the temperature and pressure settings, the feeding systems, and the control system. The latter is an important element of the unit which is fully automated (Figure 4).



PI040 5.8 mbar
TI082 17.0 °C
DPI003 0.1 mbar
TI081 18.4 °C
TI080 17.6 °C
PI041 4.1 mbar
TI090 18.0 °C
TI091 18.8 °C
TI101 16.5 °C
TI100 16.5 °C
FIS004
XV010

Figure 4. Screenshot of the control software for the the stripper.

1.4 Design and testing of the liquid injector for thermally labile feeds

1.4.1 General considerations

Injection of a thermally labile pyrolysis oil into the high-temperature downer of the CORE unit is challenging as the vapour may char and thus block the injection line. A dedicated nozzle was identified as an attractive tool to inject a thermally labile liquid. Work carried out in this task can be distinguished into three subtasks: first part of this task was to test the injector nozzle with water, ethanol and stabilized pyrolysis oil to tailor the spraying. The next step was to design and fabricate a suitable adapter to test injection into a heated device, mimicking real life operation. The third part was to test the nozzle to inject a liquid feed into a heated reactor at 600 °C.

1.4.2 Spraying liquids

The nozzle was used to spray three liquid streams, water, ethanol and stabilized pyrolysis oil. The viscosity of the water and ethanol is much lower than that of the stabilized pyrolysis oil and not surprisingly, ethanol and water could be sprayed into a fine mist. However, stabilized pyrolysis oil was a more challenging liquid stream and could be sprayed to fine droplets which were collected in a glass vial as shown in Figure 5. Thus spraying even viscous liquid such as stabilized pyrolysis oils is possible and its spraying can be improved by using a gas flow to transport the fine mist formed, which will be the target of the second subtask.

Figure 5. Spraying stabilized pyrolysis oil.

1.4.3 Adapter development

The next step was to design and fabricate a suitable adapter to test injection into a heated device, mimicking real-life operation. An adapter made out of aluminum was fabricated at RUG and enables connecting the nozzle to a reactor using a ¼″ Swagelok connection. To transport the liquid droplets, a gas stream of inert nitrogen was added and this is aimed to prevent the droplets from sticking to the walls of the adapter.

The nozzle has a preferred temperature < 80 °C and thus cannot be directly installed on a heated reactor up to 600 °C. A suitable cooler is needed to limit the temperature increase of the electronic components within the nozzle. A water cooler was added between the reactor at 600 °C and the nozzle (see Figures 6 and 7), and the nozzle temperature was monitored overnight using a thermocouple. The temperature of the nozzle did not increase past 29 °C, and thus assumed safe for the electronic components present in the nozzle.

Figure 6. Picture of the adapter and water cooling segment fabricated at RUG to attach the nozzle to a heated reactor.

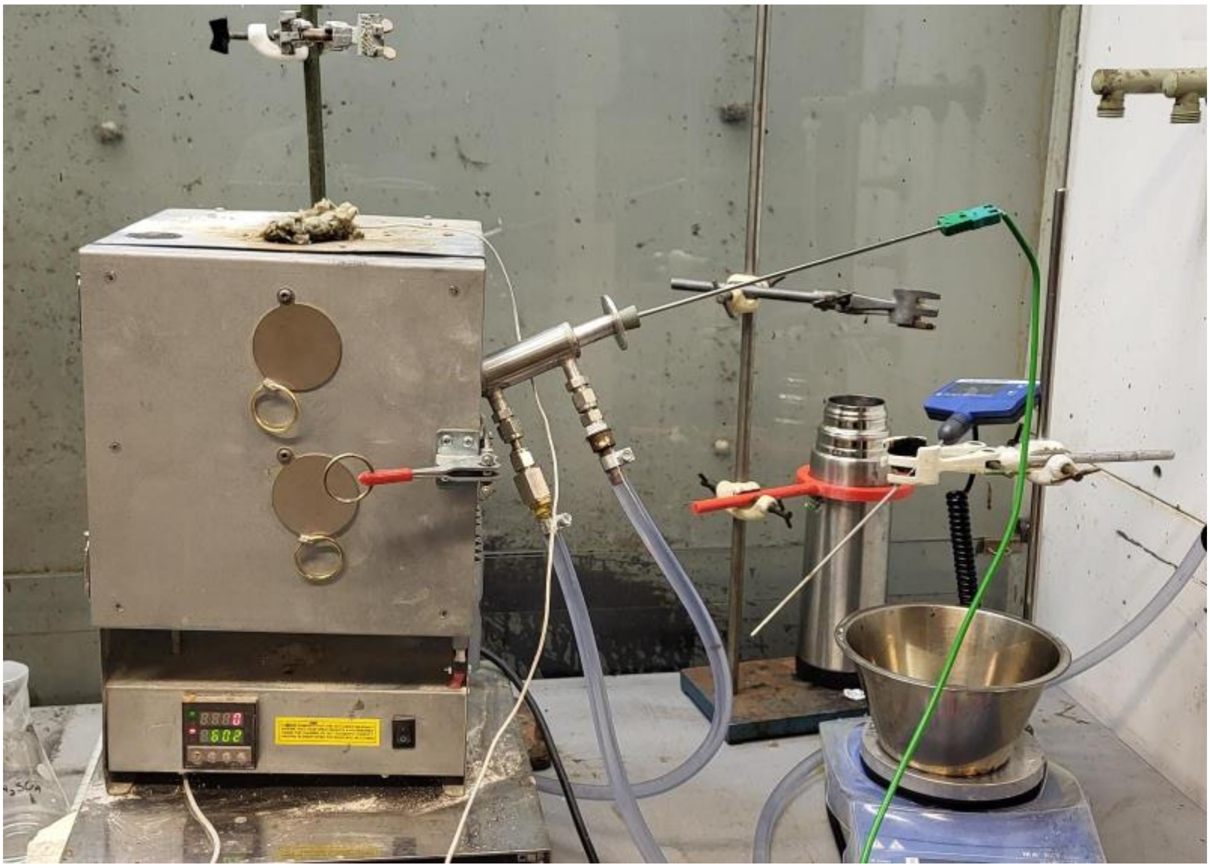


Figure 7: Picture of the test setup used to measure the temperature of the nozzle when connected to a reactor at 600° C.

1.4.3. Actual high temperature testing

The last step of this task was to test the nozzle to inject liquids into a reactor at 600°C. Three liquids were used: water, ethanol, and stabilized pyrolysis oil, and they were fed to the nozzle using a syringe pump at a constant flow rate of about 1 mL/min. A typical experiment involved feeding about 30 mL of liquid to the nozzle. The nitrogen flow rate of 150 mL/min was added to help transport the fine droplets formed and its flow rate was controlled using a mass flow controller. A collection vessel placed inside an electric oven at 600 °C was simulating the heated reactor. Evaporated liquids were separated from the nitrogen added by using a gas bottle outside the reactor outside as a gas-liquid separator. A simplified schematic of the setup used is shown in Figure 8.

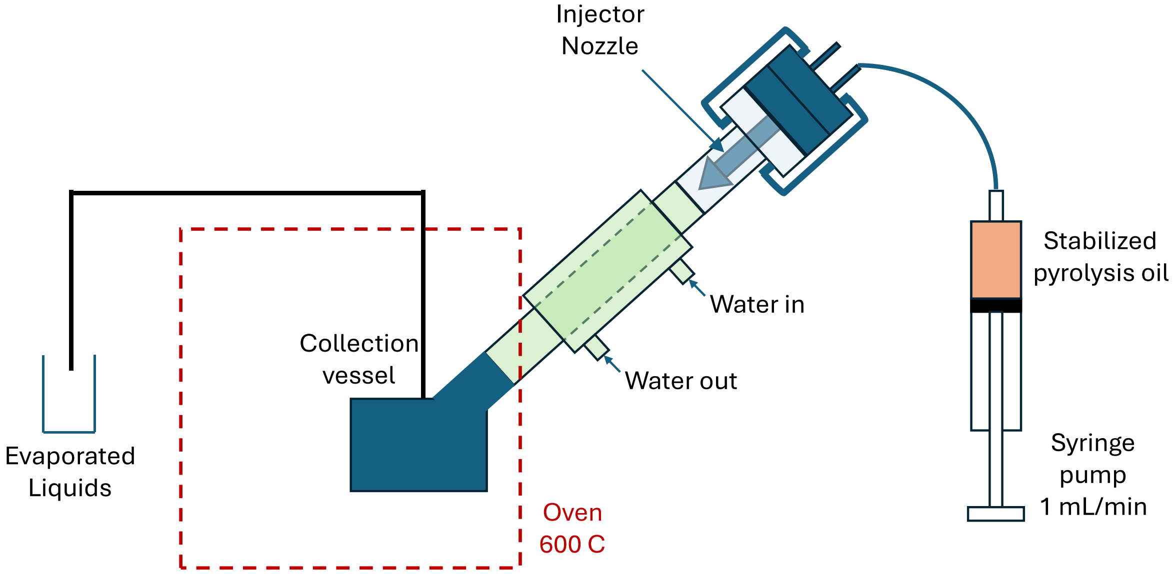


Figure 8: A simple schematic of the test setup designed to check the injection of liquids using an nozzle to a heated reactor at 600°C.

Product yields were calculated based on the equations shown below:

$$\text{Injection yield} = \frac{\text{mass of liquids collected in the collection vessel} + \text{mass of evaporated liquids}}{\text{total mass of liquid injected}} \% \quad (1)$$

$$\text{Injection loss} = 100 - \mathit{injection\ yield} \quad (2)$$

To verify the successful operation of the nozzle, its injection yield was defined based on the mass of the feed that reaches the collection vessel. Liquids that are not successfully transported to the collection vessel are usually stuck to the walls of the nozzle adapter and condenser and are thus undesirable. Since measuring this loss is challenging, it was defined as an inverse of the Injection yield. The injection yields and losses for the three liquid feeds used are shown in Table 1.

Table 1: Injection yields from the spraying experiments performed using different liquid feeds.

Liquid feed	Injection yield (wt%)	Injection loss (wt%)
Water	80	20
Ethanol	88	12
Stabilized pyrolysis oil	28.7	71.3

The nozzle gave high injection yields for low viscous liquids such as water and ethanol (80 and 88 wt% respectively) while the injection yield dropped significantly to 28.7 wt% when more viscous stabilized pyrolysis oil was used. The droplets formed with stabilized pyrolysis oil are slightly bigger than that of water or ethanol, and as a consequence stick to the walls of the cooler and the nozzle adapter, thus lowering the injection yields. Increasing the flow rate of the nitrogen gas had a limited impact on this loss, as injection yields did not increase when the gas flow rate was increased from 150 to 250 mL/min. The distance between the injection nozzle and the reactor is simply too long and this allows the accumulation of the droplets in the walls of the cooler. Some modifications of the nozzle that could increase its yields are using a much shorter water cooling segment and changing the shape and length of the injection nozzle. The nozzle currently used in this study was a conical nozzle which helps spraying the liquids into a broader mist. Needle-type of injectors could help produce a narrower mist which may be easier for the nitrogen stream to transport to the reactor. Using a longer nozzle might potentially be an attractive solution to seat it directly on the reactor while minimizing the temperature increase of the electronic components of the nozzle.

1.4 Experimental co-feeding studies using VGO, a bioliquid and catalyst

1.4.1. General considerations

Several experiments were performed to test the unit, including experiments with VGO only and with VGO in combination with a bioliquid, in this case, a hydrotreated pyrolysis liquid (HPO) in an 80-20 vol% ratio. The liquid feed rate was 19 g/h, and the amount of catalyst used was 200 g/h. The two liquids are miscible at room temperature and as such only the VGO feed pump was required for feeding the mixture. The catalyst used was an e-cat from Albemarle. The experiments were done in a 'once through' mode, without catalyst regeneration. The buffer was filled with enough catalyst to run for 3 hours, but the spent catalyst was kept in the stripper for the entire duration of the experiment. The catalyst was removed from the stripper the next day when the system was cold. Before a subsequent, fresh catalyst was added to the buffer vessel.

1.4.2. Experimental details.

Figure 9 gives a schematic overview of the downer part of the unit and the locations of the various thermocouples. The catalyst is transported from the butter to the catalyst inlet on top of the reactor. It then falls through the reactor to the stripper, in close contact with the VGO/bioliquid vapor.

The buffer vessel was filled with 800 grams of fresh catalyst. Before the start of an experiment, the top and bottom ovens were heated to operating temperature. This takes around 5 hours. The buffer and stripper vessel are supplied with 1 NL min^{-1} nitrogen flow. The catalyst is preheated in the buffer to 550°C. The stripper vessel is kept at 510°C. The liquid feed is heated to 85°C in the storage vessel under a nitrogen atmosphere. The tracing on the reactor was kept at 520°C. When the system is at operating temperature, the catalyst feed is started to feed the catalyst at the desired flow rate (200 g. h.$^{-1}$) After a few minutes, a rise in pressure over the bed in the stripper indicated that catalyst is falling through the reactor. At this point, the liquid pump was turned on, feeding the liquid at a rate of 19 g/h. The liquid in the condensers was collected for the duration of the experiment and both fractions were combined and considered the liquid product. At specific times, a sample from the gas stream exiting the stripper was taken using a syringe. The sample was then analyzed for CO, CO_2, and C1-C3 gases.

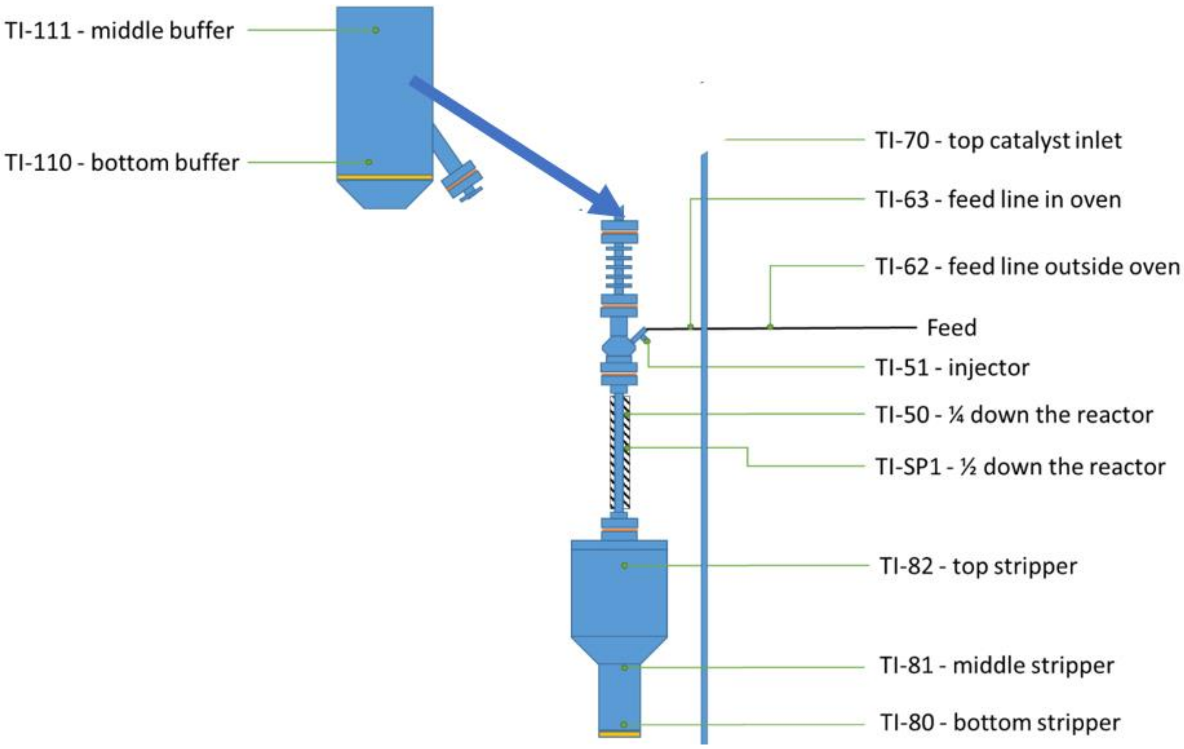


Figure 9. Schematic representation of the downer part of the unit

1.4.2. Results and discussion

1.4.2.1 Operational findings

Operation of the unit was smooth and no major experimental and operational hick ups were encountered. This is also illustrated by the temperatures at various positions in the unit for both feeds (Figures 10 and 11). The temperature of the feedline inside the oven is slightly fluctuating. This is probably caused by (partial) boiling of the feed. The point where the catalyst enters the reactor is around 20 cm higher than where the feed is introduced. A drop in temperature of around 50°C is observed between catalyst introduction and liquid feed. Another indication for smooth operation is the temperature in the buffer and stripper vessel, see Figure 12 for the VGO runs. The temperature in the buffer is again stable. In addition, the pressure drop over the bed in the buffer (red) and the stripper (blue) is also provided. The dashed vertical lines indicate the start and stop of the liquid feed. The pressure drop in the buffer vessel slightly fluctuates at the start of a run but stabilizes and shows the expected profile.

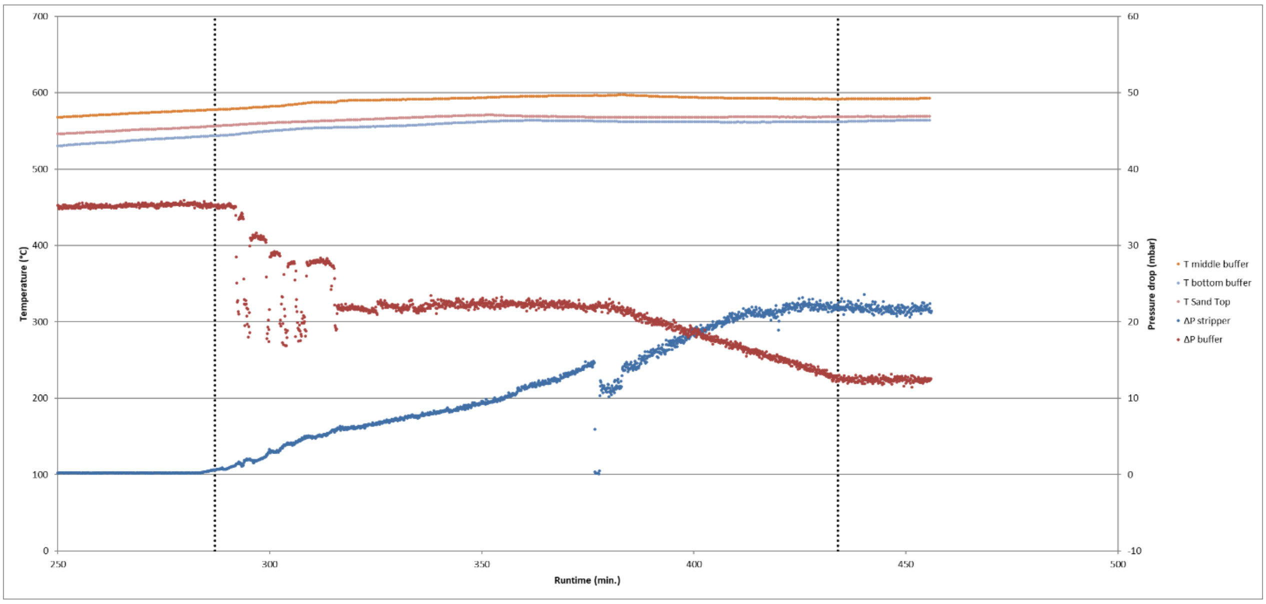


Figure 10. Pressure drop over buffer and stripper, and temperature in the buffer (VGO run).

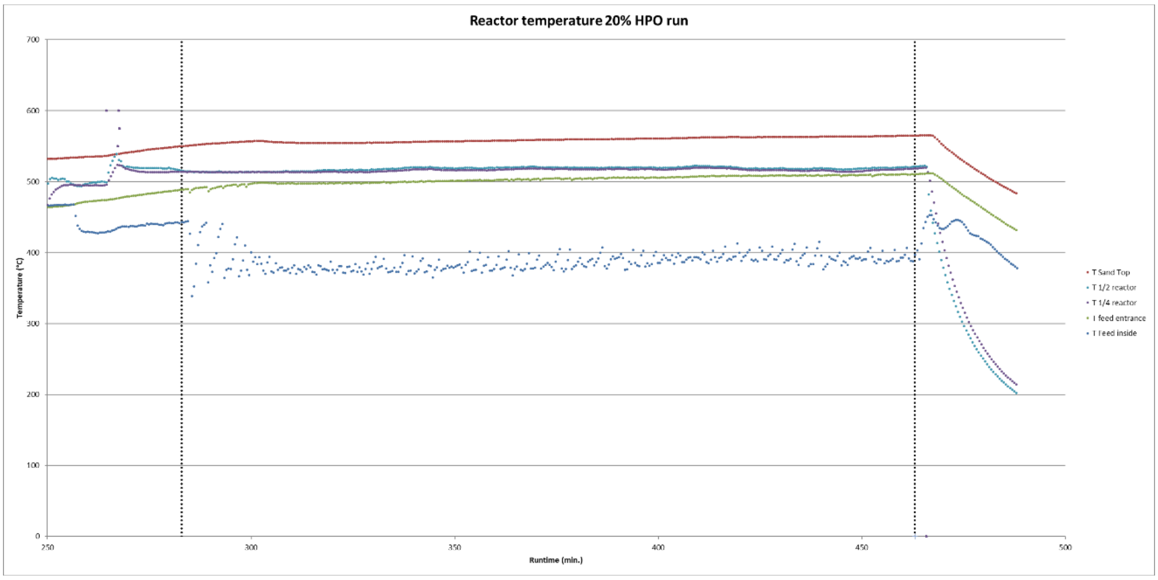


Figure 11. Temperature in the reactor for the 20% HPO run.

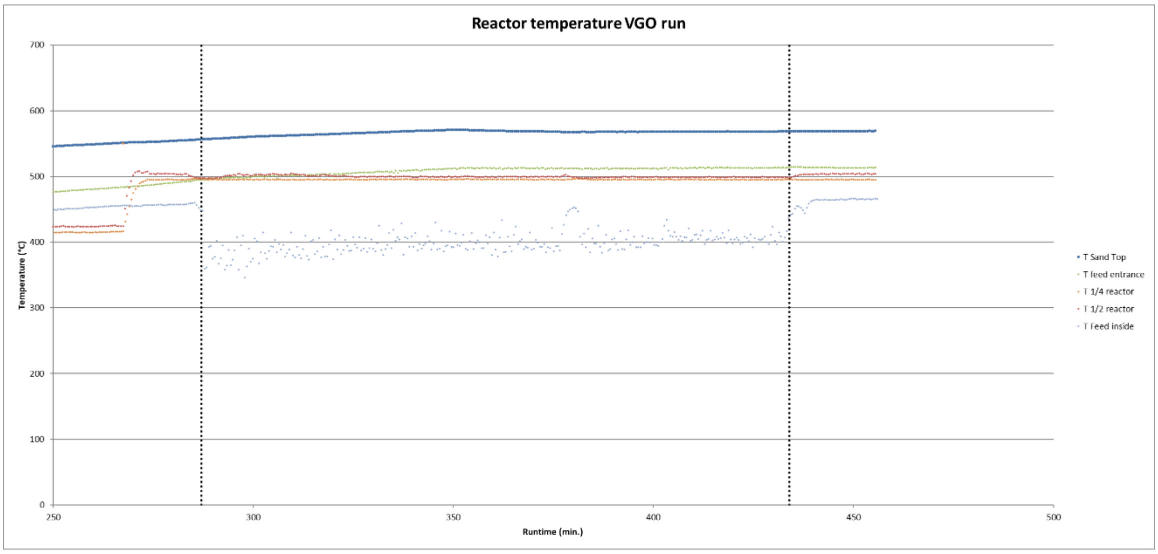


Figure 12. Temperature in the reactor for the VGO run.

1.4.2.2 Gas phase yield and analysis.

Permanent gases were analyzed with a TraceGC-1200 gas chromatograph with a TCD detector. The gas yield was 23% wt for the run with 20% HPO and 17% wt for the run with VGO. The concentrations of gas phase components for both runs with VGO and VGO/HPO are given in Figure 13. Main gas phase components are ethene and propene. The remainder is mainly nitrogen, the gas used for the fluidization of the stripper. Some peaks corresponding to (uncalibrated) higher hydrocarbons were also observed.

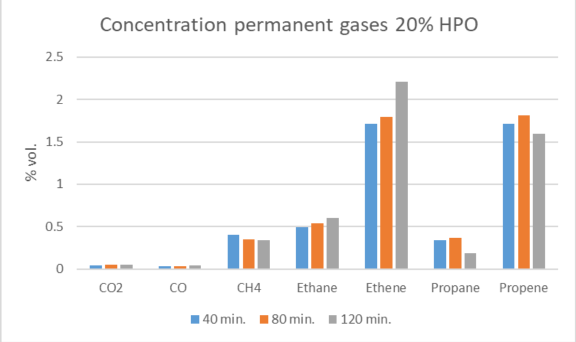


Figure 13a. Product gas composition for the 20% HPO run.

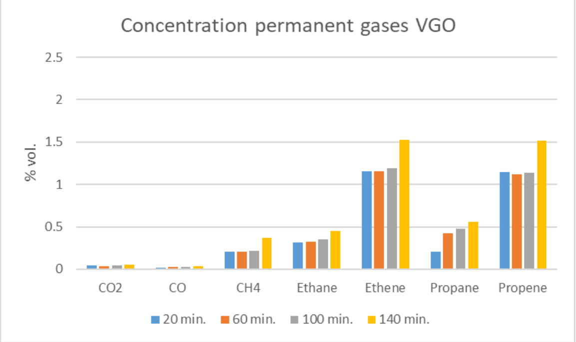


Figure 13b. Product gas composition for the VGO run.

The amount of nitrogen in the stream is around 1 NL min^{-1}. With this number, a rough estimate can be made for the gas yield of the reactions. The total yield is 23% wt for the experiment with 20% HPO and 17% for the VGO-only experiment (Figure 14).

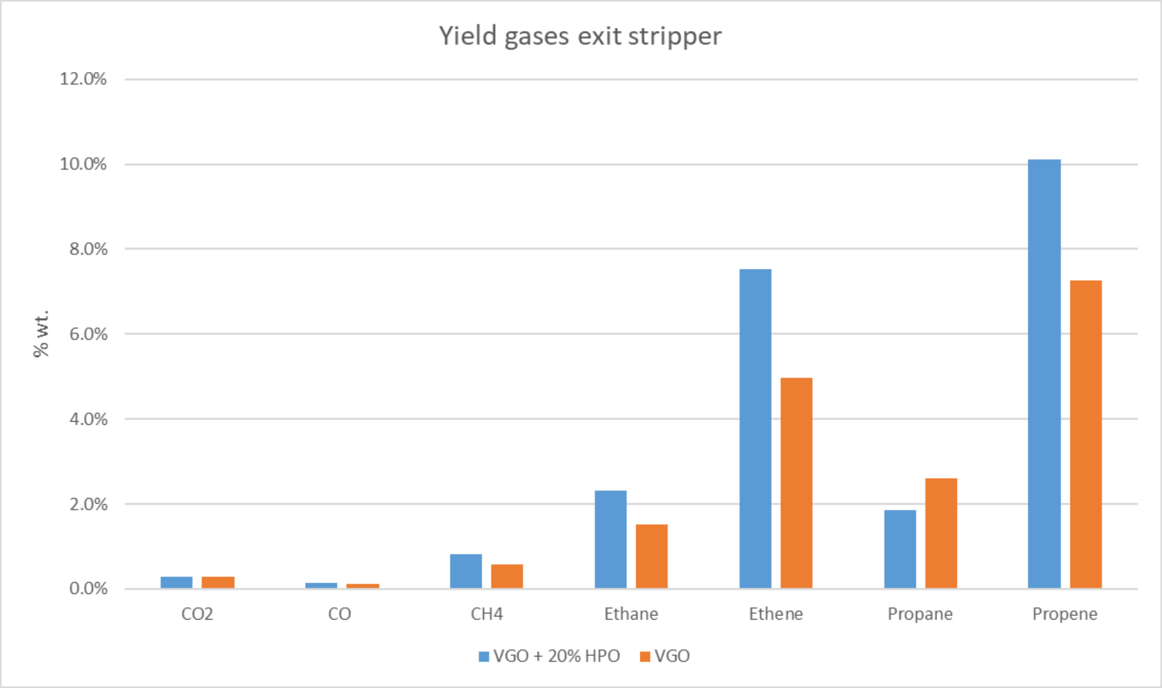


Figure 14. Estimated gas yields for experiments with VGO and VGO/HPO mixtures.

1.4.2.3 Liquid phase analysis.

The liquid composition for runs with VGO and VGO/HPO was analysed using GC-MS and the results are given in Figure 15.

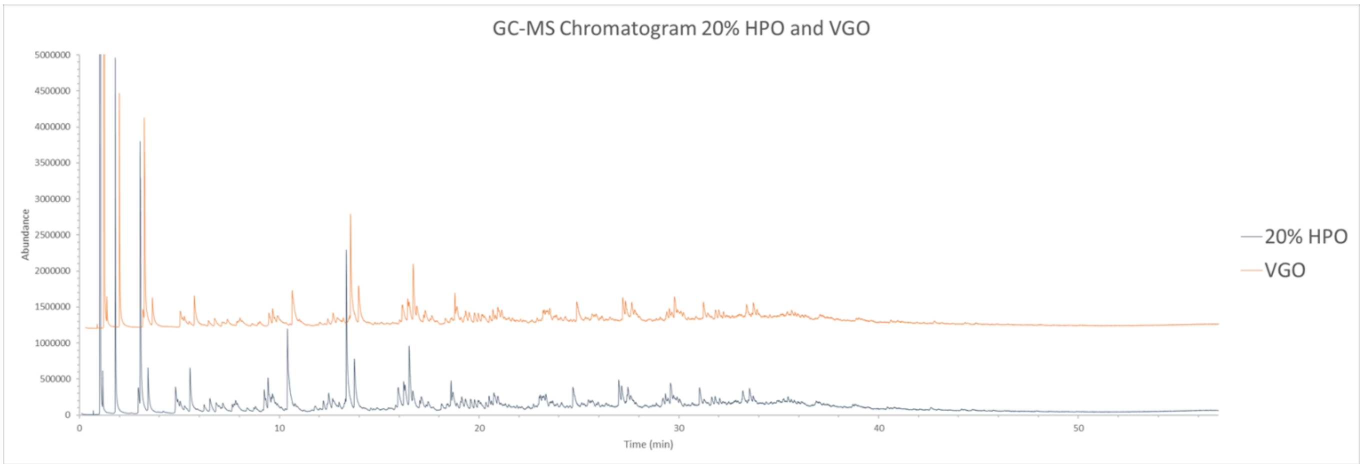


Figure 15. GC-MS analyses of the liquid phase for experiments with VGO and VGO/HPO mixtures.

The main components according to the MS library are substituted aromatics like BTX, naphthalenes, and anthracenes, see Table 2 for details.

Area %	20% HPO	Area %	VGO
8.7	p-Xylene	8.5	p-Xylene
7.1	Naphthalene, 1-methyl-	6.5	Naphthalene, 2-methyl-
6.0	Toluene	5.3	Toluene
5.2	Naphthalene	3.7	Naphthalene
3.1	Naphthalene, 2,3-dimethyl-	3.5	Naphthalene, 2,3-dimethyl-
3.0	Naphthalene, 2-methyl-	2.9	Naphthalene, 2-methyl-
2.7	Benzene, 1,2,3-trimethyl-	2.1	Benzene, 1,3,5-trimethyl-
2.5	Naphthalene, 2,7-dimethyl-	2.0	o-Xylene
2.2	Benzene, (1-methyl-2-cyclopropen-1-yl)-	2.0	Pyrene, 1-methyl-
2.1	Benzene, 1,3-dimethyl-	2.0	Phenanthrene
1.9	Naphthalene, 2-ethyl-	1.9	Naphthalene, 2-ethyl-
1.9	Benzene, 1-ethyl-2-methyl-	1.8	Naphthalene, 1,5-dimethyl-
1.9	Benzene, 1-ethenyl-4-ethyl-	1.8	Naphthalene, 1,6-dimethyl-
1.7	Benzene, 1-ethenyl-3-ethyl-	1.7	2-Methylindene
1.7	Anthracene	1.7	Pyrene, 4-methyl-

Table 2. Composition of the liquid phases for experimenst with VGO and VGO/HPO mixtures according to GC-MS.

The liquid yields were below par and this is indicative of insufficient cooling capacity of both condensers. Modifications have been proposed and will be implemented to increase the cooling capacity to maximize liquid yields.

1.4.3. Conclusions

We have demonstrated that it is possible to use and operate the novel co-FCC unit for VGO and VGO/HPO mixtures. The unit can reach the desired temperatures and the catalyst transported with a stable flow rate for a long time. The experiments yielded good insights into the performance of the downer unit and provided confidence for the next steps in the experimental program among others involving full circulation and regeneration of the catalyst and injection of thermally more labile bioliquids using the in-house developed cooled injector.

2. Development of improved catalysts and fundamental knowledge regarding catalyst performance

The objective of this project is to develop improved FCC-type catalyst materials for oxygen-containing feeds, such as pyrolysis liquids derived from biomass. Even though research in the academic setting focuses mainly on solid catalysts in the form of fine powders, their industrial application often requires the implementation of shaped catalyst bodies (e.g., extrudates and spheres). Shaping and formulation offer various advantages in the catalytic processes, such as preventing high-pressure drop phenomena and enhancing heat conductivity, as well as increasing thermal and mechanical resistance against sintering, phase transition, attrition, and fracture. On the other hand, they introduce complexity and unwanted effects on the active phase, which have to be understood and circumvented by proper catalyst processing. Formulation and shaping can be achieved when an active catalyst material, e.g., zeolite, is mixed with a binder material, like alumina, silica and/or clays, other additives, and water. The resulting shaped catalyst can have various shapes, such as extrudate and/or sphere among other shapes. The size of the shaped catalyst material can vary from hundreds µm to cm, which has a major impact on mass and heat transfer phenomena during catalytic processes. As a result, controlling those phenomena by changing the macroscopic catalyst shape is important for the design of improved catalyst materials for renewable feedstocks. Furthermore, chemical composition of the catalyst materials can also be the key to catalyst's performance. Thus, it is essential to understand the physicochemical properties of the catalyst materials in order to synthesize better catalyst for feeds with higher oxygen content. All in all, in this study, two different shaping methods were used, such as the extrusion process and spray drying, resulting in two different types of shaped catalyst bodies (i.e., extrudates and spheres). Moreover, binary extrudate catalyst materials consisting of a zeolite ZSM-5 active phase and a binder material (i.e., bentonite, kaolinite, montmorillonite and boehmite) were synthesized using an extruder while FCC-type catalyst materials were made consisting of zeolite Y and a mixture of Al_2O_3, SiO_2, and kaolinite as binder materials using a spray dryer. To achieve a better understanding of the effect of the binders in the physicochemical properties of the catalyst materials, binary catalytic systems were made in the form of extrudates. Zeolite ZSM-5 (MFI framework) was chosen as an active phase mixed with different binder materials. Initially, the binder materials were varied between bentonite, kaolinite, montmorillonite and alumina precursor (boehmite). It was found that altering between different binders has a major effect in the pore architecture of the catalyst materials, as shown in the images in Fig. 16a. Furthermore, Ammonia Temperature Programmed Desorption (NH_3-TPD) was used to unravel the changes in the acid sites of the samples, as illustrated in Fig. 16b. It was noted that the binder has a great impact on the acid sites. Comparing the samples in which different clays were used (e.g., bentonite, montmorillonite, and kaolinite) to the alumina binder material, it is seen that clay binder materials resulted in weakening of acid sites and in some cases (i.e., bentonite and kaolinite) loss in acidity. These phenomena can be attributed to pore blockage phenomena as well as migration of cations from the clay binder materials to the zeolite phase material.

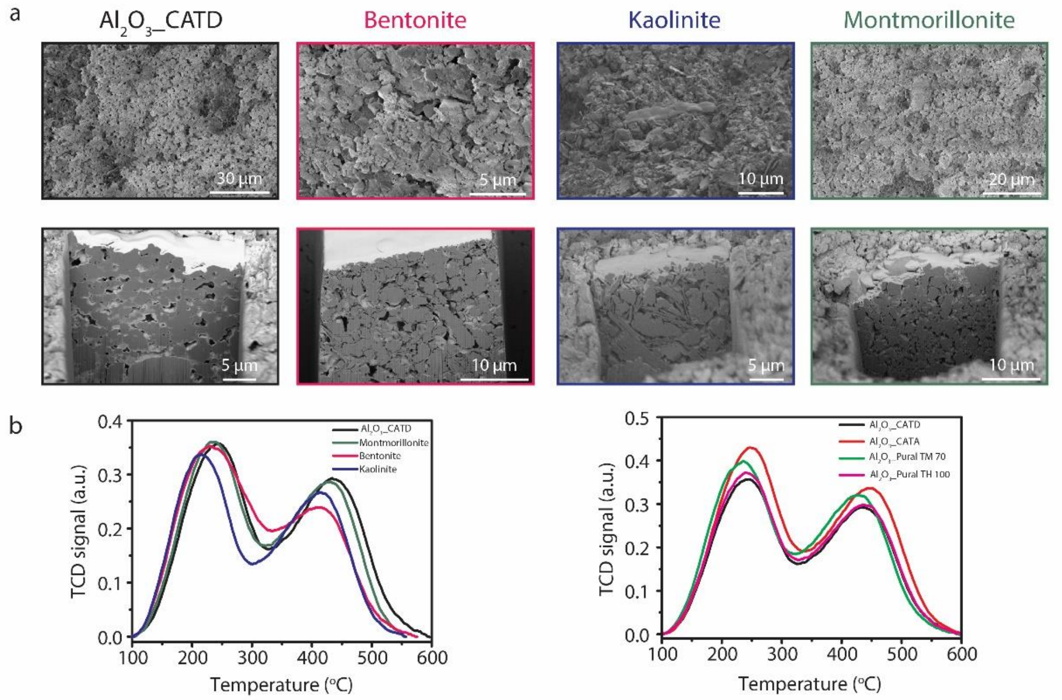


Figure 16 Physicochemical characterization of the extrudate catalyst materials used in this study. a) (top) Scanning Electron Microscopy (SEM) and (bottom) Focused Ion Beam – Scanning Electron Microscopy (FIB-SEM) images obtained for the binary extrudate catalyst material samples with different binder, such as Al_2O_3_CATD (black), Bentonite (red), Kaolinite (blue), and Montmorillonite (green). b) Ammonia Temperature-Programmed Desorption (NH_3-TPD) analysis of the binary extrudate catalyst material samples with different binder (left), such as Al_2O_3_CATD (black), Bentonite (red), Kaolinite (blue), and Montmorillonite (green), as well as different alumina binders (right), such as Al_2O_3_CATD (black), Al_2O_3_CATA (orange), Al_2O_3_Pural TM 70 (green), Al_2O_3_ Pural TH 100 (pink).

Moreover, the influence of the alumina binder materials on the acidity of the extrudate catalyst materials was studied by choosing different alumina binder precursors (boehmite) materials. Different boehmite materials were chosen with varying porosity and crystallite size. It was shown that alumina precursor's properties can have an important impact on the acidity of the extrudate catalyst samples.

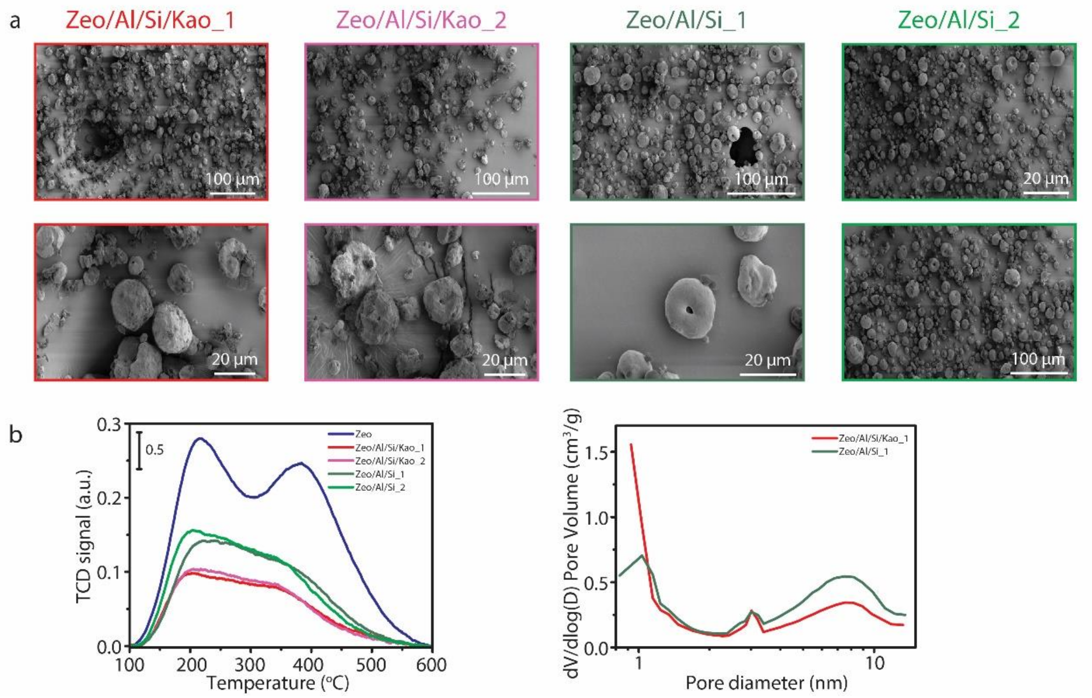


Figure 17. Physicochemical characterization of the Fluid Catalytic Cracking (FCC)–type catalysts used in this study. a) Scanning Electron Microscopy (SEM) images obtained for the FCC-type catalyst material samples with different binder composition, such as Al_2O_3-SiO_2-Kaolinite (Zeo/Al/Si/Kao_1, red & Zeo/Al/Si/Kao_2, pink) and Al_2O_3-SiO_2 (Zeo/Al/Si_1, dark green & Zeo/Al/Si_2, light green). b) (left) Ammonia Temperature-Programmed Desorption (NH_3-TPD) analysis of the FCC-type catalyst material samples with different binder composition, such as Al_2O_3-SiO_2-Kaolinite (Zeo/Al/Si/Kao_1, red & Zeo/Al/Si/Kao_2, pink) and Al_2O_3-SiO_2 (Zeo/Al/Si_1, dark green & Zeo/Al/Si_2, light green), and Zeolite Y reference sample, (right) Pore volume distribution obtained from Ar physisorption measurements for the FCC-type catalyst material samples with different binder composition, such as Al_2O_3-SiO_2-Kaolinite (Zeo/Al/Si/Kao_1, red) and Al_2O_3-SiO_2 (Zeo/Al/Si_1, dark green).

In a next step, further studies on the matrix effects in FCC-type catalyst materials were performed. FCC-type of catalyst materials with different binder materials were made using a spray dryer. Aiming to synthesize a FCC-type catalyst which it would be similar to the samples currently used in oil refineries during FCC process, a sample was made using zeolite Y (FAU framework) as the active phase and a mixture of Al_2O_3, SiO_2, and kaolinite as binder materials (further noted as Zeo/Al/Si/Kao). The latter sample was compared to a sample in which only Al_2O_3 and SiO_2 were used (further noted as Zeo/Al/Si). It is noted that the presence of kaolinite affects the morphology as well as the size of the catalyst particles of FCC-type catalysts, as shown in Fig. 17a. It is important to mention that Zeo/Al/Si consists of the same zeolite content compared to Zeo/Al/Si/Kao while kaolinite was replaced with Al_2O_3 and SiO_2 in the same ratio. Furthermore, by comparison of Zeo/Al/Si/Kao and Zeo/Al/Si samples, it is found that the overall acidity increases, as shown in Fig. 17b (left). The latter can be attributed to higher content of Al_2O_3 binder as it can contribute to weak and intermediate in strength acid sites. Moreover, replacing kaolinite with Al_2O_3 and SiO_2 can explain also the increase in strong acidity to higher porosity of the binder which could enhance accessibility to the smaller pores of the zeolite, as it can also be seen by Ar physisorption in Fig. 17b. The presence of kaolinite could also result in a decrease in the number of acid sites due to the migration of cations to zeolite. Last but not least, the effect of the changes in the parameters during the spray drying procedure is studied. It was shown that it can affect the morphology of the FCC-type catalysts as well as their acidity, as illustrated in Fig. 18.

Overall, two different types of shaped catalyst bodies were investigated, such as extrudate and spray-dried catalyst materials, were developed for the oxygen-containing feedstocks. Composition of the shaped catalyst bodies is the key to performance and to the knowledge to optimize the co-processing of vacuum gas oil and biomass-derived pyrolysis liquids. In depth and advanced characterization was performed to obtain more insights on the effect of the extrudate and FCC-type catalyst materials. It was revealed that the composition of the catalyst need to be chosen based on the desired physicochemical properties. Certain delays in the delivery and installation in the spray dryer and Pyrolysis Gas Chromatography-Mass Spectrometry (Py-GC-MS) delayed the small scale testing and the development of more catalyst materials.

3. Integration studies (BTG)

The objectives of WP4 were to collect data from previous work (incl. WP2 and WP3) and analyse several technical aspects.

<u>Task 4.1. Processing synergies.</u> The data set available for co-processing pyrolysis liquids and VGO will be updated and further analyzed to provide first some empirical insights in the synergetic effects of PL. Based on the expected reliable operation of the lab unit, the extensive set of operating data and the increasingly better idea on the quality of pyrolysis liquids in relation to co-FCC, much more insight will be generated in the more mechanistic pathways for the coprocessing of such bio-liquids.

Limited tests have been performed in the constructed downer unit itself. However, around 10 data sets became available from other projects where BTG was involved in institutes and research organizations based on which analysis could be done. These (research) projects included results from a variety of projects, EU funded, national and international bi-lateral cooperations, and commercial projects. Also (limited) information is available on the commercial trials in Sweden by Preem, and on semi-commercials done by other third parties.

Unfortunately, most results and information from these works are confidential as of date, while some are restricted as research papers will be prepared. Overall, the addition of pyrolysis oils to VGO using conventional catalysts does not alter conversion and yields of combustible gas, coke, LCO and decanted oil significantly provided that the substitution ratio is below 5 wt.%. Some decrease can be seen in the yield of LPG and its components with a respective increase in gasoline yield. A small increase in methane and ethane is typically seen, and a drop in hydrogen. The latter is attributed to hydrogen consumption in other reactions, as hydrogen transfer reactions between two hydrocarbons or carbohydrates will take place, through two consecutive reactions of dehydrogenation and hydrogen.
Recent results included work on the oils in an in-house developed unit with some similarities to the Core unit. A rather recent paper from which data could be extracted (and publicly available) is one from TU Vienna.[1] The oils were provided by BTG, and both, untreated, mildly treated, and more severely treated oils from pinewood were used. The different bio-oils were all processed in as co-feed with VGO in admixture of 95 wt % VGO and 5 wt % bio-oil. Firstly, the addition of bio-oils led to a minor decrease in conversion in comparison to the use of pure VGO (∼1−1.5 wt %) and also to an increase in the produced amount of coke (∼1 wt %). This is partially due to the lower amounts of moles of carbon that is fed into the reactor system. Expectedly, a (more severe) treatment of the oils led to a larger decrease in gas production, an increase in liquid yields and a rise in the specific gasoline fractions.

An increase in carbon dioxide is clearly observed: this can be attributed to the decarboxylation of the acids and ketones present in the pyrolysis oils. Aldehydes may undergo decarbonylation and carbonylation on zeolites at low temperatures. Limited CO is noted, probably while the "shift" reaction converts it to form CO_2 and hydrogen. Water formation is observed as the oxygenated compounds undergo dehydration reactions on zeolites. The water yield seems to pass through a maximum with increased conversion. The decreased

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[1] file:///C:/Users/rhv20/Downloads/lutz-et-al-2022-wood-derived-fast-pyrolysis-bio-liquids-as-co-feed-in-a-fluid-catalytic-cracking-pilot-plant-effect-of.pdf

water yield in high conversions may be associated with the consumption of water in other reactions such as "shift" and reform.

Task 4.2. Deactivation. *Deactivation studies will lead to relationships between initial and spent catalyst acidity and reactivity, as well as pore accessibility versus reactivity versus both, reversible and irreversible, deactivation pathways. This eventually will lead to recommendations in terms of bioliquid's characteristics (for example untreated versus treated PL), versus required refreshment rates.*

Task 4.3. Modelling. The performance of FCC co-processing will be modelled in flowsheets in terms of both, the unit operation as well as refinery operation. This comprises two separate subtasks:
a) In a freeware program – CoCo simulation - the co-FCC of pyrolysis liquids will be modelled as a separate unit operation. It is known already that such flow sheeting programs (for example Aspen) heavily rely on individual reaction kinetics of feed and intermediate products and are not yet capable of modelling oxygenated compounds. While obtaining detailed correlations go far beyond the scope of the project (and likely requires a number of PhD students), simpler models based on 'grey box' approaches will be established.
b) Due to the introduction of 'alien' materials in the co-processing, and in particular CO and CO_2 *from the FCC, together with synergetic effects on the overall yields (for example lowering the LPG and* H_2*), the consequences on the overall refinery performance will need to be established in a holistic approach, starting with a 'standard' type of refinery complex (although there isn't). Typically, the concept will be addressed in relation to student's assignments (traineeship, bachelor or master's degrees or similar).*
The flow sheeting programs will be presented as Open Access materials, for example in the CoCo' example database.

The co-processing of bio-oil and vacuum gas oil (VGO) in a FCC riser reactor is studied. Literature reports that co-feeding bio-oil is feasible without changing the yield structure of the product significantly. Demonstration scale experiments and analyses show that up to 10 wt% of bio-oil can be co-processed. At 5 wt% of bio-oil co-fed, there are even synergetic effects when looking at the yield structure. More valuable products like gasoline and LCO and less undesired products like coke and dry gas are produced. The optimal set-up for feeding bio-oil is to feed the bio-oil at the bottom of the riser, where the temperature and catalyst to oil ratio are higher than elsewhere in the reactor. The VGO is injected at a higher position. This causes the largest biomolecules to be cracked thermally, while they would not vaporize as well if the bio-oil and VGO were fed at the same height. A significant amount of oxygen does not leave the reactor in the form of CO, CO_2 or H_2O. Analysis of the naphtha product of a demonstration scale co-processing set-up show that phenolic compounds are present, but that their quantity is not high enough to cause problems with the fuel.

FCC co-feeding studies have been reported in the literature. For example, successful co-feeding of 15 wt% of biocrude oil, containing about 25 wt% of oxygen (Agblevor et al.). Hardly any change in the yield structure of the product is observed and the fuel produced contains negligible amounts of oxygen, which is thought to be the result of hydrogen transfer between the VGO and bio-oil. Gasoline and LCO yields increase marginally when co-feeding bio-oil, while the coke yield is decreased. Co-processing 20 wt% of bio-oil may be a limit (De Rezende

Pinho et al.) as co-processing higher amount of bio-oil leads to too excessive coke formation. The yield structure of the product looks almost identical to that of regular VGO processing and the hydrocarbons obtained are reported to be almost oxygenate-free. The dry bio-oil co-feeding resulted in a low liquid product yield compared to the other two oils. et al. co-fed an untreated bio-oil to a demonstration scale FCC unit. Yields similar to the cracking of pure VGO were reported for the co-processing of 10 wt% bio-oil, while co-feeding 20 wt% led to deterioration in yield structure. There may also be a significant amount of phenols in the naphtha range of products. Deviations between this study and other literature most likely stem from the fact that in other literature, laboratory-scale reactor are used instead of a demonstration-scale FCC unit. Another big advantage of co-feeding on a much larger scale is that the bio-oil and VGO can be introduced into the riser at different heights. At the bottom of the riser, the temperature and catalyst to oil ratio are significantly higher than elsewhere in the reactor. Introducing the bio-oil first gives the largest molecules the chance to be cracked thermally, thereby creating smaller molecules that can enter the catalyst particles to be cracked catalytically. The VGO is then introduced somewhat higher in the riser. If the large bio-oil molecules are not cracked thermally first, they will not vaporize completely, leading to coking on the catalyst particles. A more recent study by the same authors compares the co-feeding of 5 wt% and 10 wt% fast pyrolysis oil. It is again shown that co-processing 10 wt% of bio-oil is technically feasible. The amount of oxygenates, like phenols, in the product increases with increasing amounts of bio-oil processed. The data presented in this paper suggests that co-feeding only 5 wt% even has a positive effect on the yield structure, meaning more gasoline and VGO is produced, while less coke and dry gas is produced. Schuurman et al. tried to eliminate the costs that occur from hydrodeoxygenation by replacing this step with a less energy intensive one. A catalytic pyrolysis oil is compared to a deoxygenated oil in terms of co- feeding yield structure. It is shown, on a lab scale, that the yield structures show only small differences. Wang et al. co-processed 10 wt% of bio-oil in a pilot scale FCC unit as well, leading to almost similar yields as for feeding pure VGO. A catalytic pyrolysis oil is used, which has a lower oxygen content than an untreated bio-oil made by fast pyrolysis.

The objective of this task was to model the co-feeding of pyrolysis oil (PO) with vacuum gas oil (VGO) to the riser reactor of a fluid catalytic cracker (FCC). A first model was based on a fixed conversion reactor, which used fixed yields for the output species heavy oil, diesel, gasoline, LPG, dry gas, coke, CO, CO_2 and water. The model made in this assignment is of a more predictive nature and therefore should be based on a reactor that uses kinetics, which in this case will be a plug flow reactor (PFR). In contrast to a fixed conversion reactor, a kinetic reactor allows for changing input conditions such as feed composition, residence time or temperature. In a further attempt, 6 and 10 lump kinetic models of the cracking of VGO feeds are constructed based on kinetic data found in literature. These models were constructed in a Cape-Open to Cape-Open environment (COCO), which is flow sheeting software that is available to download for free, in combination with calculations done in Excel. The 10 lump model showed a realistic yield structure and should be expanded with reaction kinetics for the co-processing of bio-oil. COCO is still a relatively undeveloped piece of software and there are some small issues encountered when modeling these systems. When these minor issues are resolved COCO looks like a solid piece of software to do basic flow sheeting simulations for co-feeding.

Nevertheless, the modeling of FCC process at this stage also shows some important drawbacks: the modeling of FCC processes requires experimental data upfront and the flow sheeting should be used to understand the experimental results from a bird's eye view, rather than predicting them *a piori*. This is due to the rather unknown and complexity of the reactions that occur in the FCC reactor, even if conventional fossil resources are used, which is further complicated by the introduction of oxygenates. In that respect, FCC flow sheeting options are available in Aspen, but the results strongly rely on a excessive data set and results from lab testing where the various cracking reactions are considered. Simpler 'grey' models have indeed been applied, describing deviations between product slates and conversions, related to the presence of the new oxygenates, and used to describe the synergies between the VGO and oxygenated compounds.

<u>Task 4.4. Green carbon balances in co-refining</u>. A specific non-technical challenge in the proposed approach of co-feeding is how to calculate the green carbon fraction in the final products. Typical ways to do this are by analysis, but this requires expensive and sometimes unreliable C^{14} analysis, or mass / carbon balance methods. Discussion are ongoing, and the mass balance and carbon balance methods proposed by the work group for co-processing at refineries. As a disadvantage, however, would provide not a completely verifiable quantification means to ensure that there will be any renewable content within finished fuel. Discussions are ongoing, and part of this Task will be to participate in these discussions and provide information, calculations and justifications for a 'better' method.

BTG actively participated in the discussion on identifying options for allocating the bio-based content, while a viable alternative to the usual Carbon14 testing – which is quite imprecise at the low levels of bio-based content - is required. In a 'CPO-project', funded by the European Commission and managed by NEN (Royal Netherlands Standardization Institute) a methodology was developed for co-processing pyrolysis oil to create and assess harmonized instructions (standard) that lays down the requirements for an allocation technique for co-processing pyrolysis oil (CPO).

The project was specifically focused on co-processing pyrolysis oils in a fluid catalytic cracker (FCC) unit, typically a central refinery unit used to upgrade heavier distillation cuts to light products (see Figure 18). The unit cracks heavier oils in the presence of a catalyst.

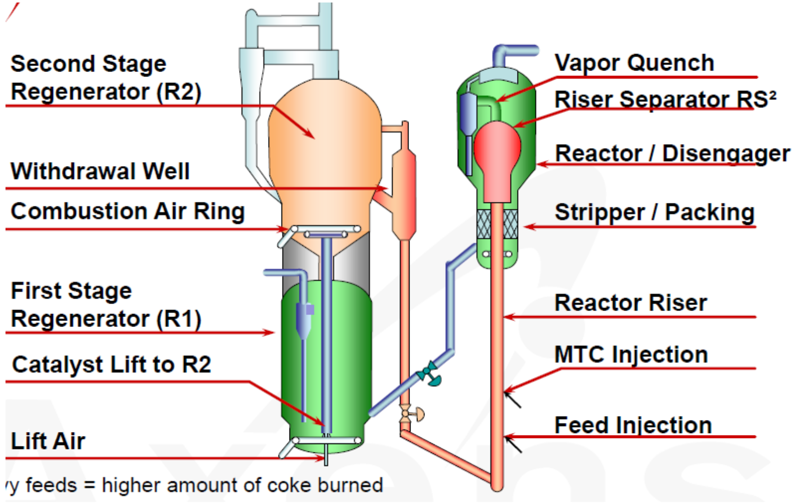

Figure 18 – Scheme of an FCC unit

Oils and residue feed are mixed with a catalyst and cracked into lighter products. The primary product is the naphtha, used in gasoline products by blending. By-products are lighter products that feed other refinery units and heavier products that is blended into diesel or recycled. In the process coke is deposited on the catalyst and blocks the cracking reaction: it is removed from the catalyst by combustion, reactivating the catalyst. In such a unit, the FPBO is likely fed by a separate injection system, being non-miscible with fossil oils. The molecules are cracked together with regular feed and the green carbon content is distributed across the products such as dry gas, LPG, gasoline, light cycle oil, diesel or marine fuel (slurry oil). Synergetic effects between the bio- and regular streams may result into nonlinearities, which makes the calculated share of renewables in the product different from the actual one, probably also inconsistent over time.
In a mass balance method, any effect of saving of fossil resources by replacing them with bio-based raw material is attributed to a certain product by accounting them through a mass balance. Various methodologies can be considered.

Total mass balance: A defined mass input from the renewable source (FPBO) is known and a mass balance over the whole unit is determined. This includes known masses from, a.o. fossil fuel and product as input, Renewable fuel and product as input, products distribution as output and feed and product densities. The share of carbon-monoxide, carbon-dioxide and water ($CO + CO_2 + H_2O$) is considered to be originating mainly from bio-source, removing this portion from whole bio-oil content.

Carbon mass balance: the mass fraction of the bio-component in the inputs to the co-processing is calculated. This is used to estimate the renewable mass fraction of the product output(s). It accounts for the loss of carbon to CO and CO_2 by a correction factor. The method requires only flow and density data but requires an accurate determination of the carbon content of the biologically based feedstock (C_{bio}). The method assumes – for simplicity reasons - that all CO and CO_2 produced in the unit originates from bio-based feedstock and that is therefore deducted from the mass of biological input. All remaining biogenic carbon is assumed to end up in the output products.

Energy balance: The bio-yield is calculated on the energetic weighted ratios of bio-based and fossil inputs. Here, the energetic weighting factor is determined based on the fraction of the energy content of the biological input on the total energy content of all relevant inputs. The energy content is based on the measurement of heating values of different raw materials. Unlike the total mass balance, this method does not require analyses of the different products and of water, CO and CO_2 or a steady operation from the unit. The renewable energy content of the bio-oil is then considered to be completely converted into all the different products in equal ratio. For each output product, the share of bio-based energy content is considered to be equal to the energetic weighted ratios of bio-based in the inputs.

Yield technique: this works on the basis of the principle that any changes in yield of a process (unit) are the result of adding the new feedstock and are considered as renewable product. The baseline scenario of only fossil feedstock is thus assessed first. One shall measure product yields under certain unit conditions for a certain amount of fossil input (e.g. 100 kg VGO). The co-processing is then done on the basis of regular feedstock plus FPBO. The product yields shall be measured under the same conditions for the same amount of fossil input (e.g. 100 kg

VGO) + the co-processed input (e.g. 10 kg FPBO). The incremental yield method does not attempt to directly measure the amounts of renewable fuel product produced. Instead, it estimates the amount of renewable fuel produced based on observing the changes in total yields when comparing co-processing scenarios to baseline scenarios with only petroleum feedstock processed.
To avoid overestimation of certain renewable products, in case the addition of biogenic feedstock gives negative yields for some other products, a correction can be applied, wherein the negative yields are subtracted from the positive ones.

Data from a downer unit tested with oils from BTG were analyzed with respect to these envisioned standards, and a dedicated final groups meeting was organized to discuss the results and final steps (sept 2022). The actual outcomes of these sessions (and results from the tests) were kept confidential at that time, and cannot be disclosed yet.